FAR INFRARED PHOTOCONDUCTORS: RECENT ADVANCES AND FUTURE PROSPECTS

E. E. Haller[1,2] and J. W. Beeman[2]
[1] Dept. of Mater. Sci. and Eng., University of California, Berkeley, CA 94720
[2] Materials Sciences Div., Lawrence Berkeley National Laboratory, Berkeley, CA 94720

ABSTRACT

The first germanium blocked impurity band (Ge BIB) detectors displaying simultaneously all the properties characteristic for this type of photoconductive device have just been reported.[1] Using a combination of bulk grown ultra-pure germanium and liquid phase epitaxy (LPE) to form the required thin blocking layer on doped absorber layer structure, Ge BIB devices with a long wavelength cut-on near 50 cm^{-1} (> 200 μm) and low dark currents have been fabricated. Excessive diffusion of the majority donor dopant (antimony) results in an unfavorable electric field distribution and low responsivity. These preliminary Ge BIB results are encouraging and they point the way for further improvements.

The move to wavelengths beyond Ge BIB detectors will become possible with n-type GaAs BIB devices. With donor binding energies near 6 meV, such BIB detectors will show an onset beyond 30 cm^{-1} (> 330 μm). Successful growth of ultra-pure epitaxial layers has been demonstrated and can be achieved routinely in our laboratories using LPE with a liquid Ga solvent. The next step is the growth of appropriately doped n-type GaAs for the infrared active layer. The use of Te donors appears promising for this purpose because of their low diffusivity and large solubility limit.

Looking beyond GaAs BIB detectors, obvious candidates for the next generation of semiconductor photoconductors are InAs and InSb. These narrow band gap compound semiconductors have donor binding energies of 1.4 meV and 0.7 meV, respectively. We expect InAs and InSb photoconductors to show response out to the millimeter wavelength region. Formidable materials problems need to be solved before InAs and InSb array development becomes feasible, but the promise of a photoconductor responding well into the wavelength range covered by bolometric detectors is highly attractive.

1. INTRODUCTION

The highly successful IRAS mission[2] marks the beginning of modern, far infrared photoconductor research and development. Photoconductors based on extrinsic semiconductors appeared to be the most promising candidates to achieve the figures of merit required for low background observations. The early efforts focused on majority and minority dopant control, formation of low noise, ohmic contacts, extension of the photoconductive onset to longer wavelength and an improved theoretical understanding of the photocurrent signal formation. Progress in all these areas has culminated in today's state-of-the-art Ge:Ga, Ge:Sb and stressed Ge:Ga photoconductive detectors and detector arrays[3-6] and quantitative, predictive models for the temporal evolution of the photocurrent with changing wavelength photon illumination.[7-9]

The need for photoconductors with longer wavelength response and for ever larger arrays drives current and future semiconductor far IR detector research and development. Ge BIB detectors are on the verge of reaching performance useful for astronomical observations. Efforts in GaAs BIB research are looking highly promising because the biggest impediment, i.e., the growth of high-purity GaAs epilayers with net-concentrations of $| N_D – N_A | < 10^{12}$ cm^{-3}, has been overcome.[10] Looking further into the future, we propose to evaluate the potential of compound semiconductors with exceptionally low effective electron masses and correspondingly small donor binding energies and large Bohr radii. InAs and InSb belong to this group of

Contact information for E. Haller: Email: eehaller@lbl.gov, phone 510 486 5294

semiconductors. While the lowest residual impurity concentrations in these semiconductors are still in the concentration range of 10^{14} cm^{-3} (too high to lead to efficient donor freeze-out upon cooling), renewed interest in these compounds and dedicated liquid phase epitaxy experiments may lead to very long wavelength semiconductor photoconductors.

In this brief review, we will focus on Ge and GaAs BIB detector research and development and on an evaluation of extrinsic InAs and InSb for far IR detector applications.

2. PHOTOCONDUCTOR BASICS: BULK SEMICONDUCTOR DETECTORS

2.1. Figures of merit and photoconductor signal modeling

The basic physics of semiconductor photoconductors has been reviewed by several authors[11-13] and it is briefly summarized here.

An extrinsic bulk semiconductor photoconductor is conceptually perhaps the simplest unipolar semiconductor device. A piece of a highly doped semiconductor single crystal is sandwiched between metallically doped ohmic contacts. At very low temperatures, the majority dopants are frozen out (neutral) except for a small fraction which is compensated by minority dopants (N_{min}). It is this small fraction of ionized majority dopants (N_{maj}^{ion}) which controls the free photocarrier lifetime τ.

$$\tau \ \alpha \ \frac{1}{N_{maj}^{ion}} \cong \frac{1}{N_{min}} \tag{1}$$

The photocarrier lifetime τ, in turn, directly affects the magnitude of the signal current I_{signal}:

$$I_{signal} = \eta e \dot{n} \tau \mu E / L , \tag{2}$$

with η = quantum efficiency, e = charge of the electron, $\dot{n}$ = photons per unit time, μ = free photocarrier mobility, E = applied electric field and L = interelectrode distance. Two numbers which are often used to characterize a photoconductive detector are the responsivity R and the noise equivalent power NEP:

$$R\ (A/W) = I_{signal}/P \text{ with P = photon power reaching the detector} \tag{3}$$

and

$$NEP \left(W/\sqrt{Hz}\right) = \text{noise/responsivity.} \tag{4}$$

In the low background limit, the noise will be dominated by the random arrival of photons at the detector and we define a background limited noise equivalent power:

$$NEP_{BL} = 2\ (P_{background} \bullet \eta\nu)^{1/2}. \tag{5}$$

The responsivity of state-of-the-art doped Ge photoconductors lies near 10 A/W. For practical purposes and because certain noise contributions are still unaccounted, one folds all the imperfections of the photoconductor response into the quantum efficiency, calling it detective quantum efficiency η_{Det}. Typical values of η_{Det} range from 10 to 30%.

According to this simple analysis, a bulk photoconductor should show a step function increase (decrease) proportional to a step function photon flux increase (decrease). However, users of photoconductors know that this is often not the case, especially at low backgrounds. The temporal evolution of the signal often has two components with distinct time constants, or it shows even more complicated dependencies. Haegel et al.[7,8] were first in explaining some of these phenomena in terms of readjustments of the space charge distribution and electric fields near the contacts. They were able to analyze the static and dynamic conditions for photon flux changes, predicting two distinct signal components with different time constants. More recently, they have generated an analytical expression for the fast, initial photoresponse.[9] This quantitative signal description combined with photoconductor signal modeling will be most useful for the analysis of the data to be generated by semiconductor photoconductors, for example in the MIPS instrument on the Space Infrared Telescope Facility (SIRTF).

2.2. Application of uniaxial stress to p-type Ge

In an effort to extend photoconductor response to longer wavelength, the change of the effective hole mass with the application of uniaxial stress is utilized.[14] The reduction of the average hole mass leads to a reduction in the hole binding energy by a factor of almost two.[15] This approach to extending the wavelength to > 200 μm proved highly effective and several far IR instruments carry (or will carry) arrays of stressed detectors.[5,6] Advanced cryogenic mechanical engineering has made possible the co-axial application of stress to sixteen photoconductors in one stack. This has led to the development of a 16×16 stressed photoconductor array discussed in detail at this workshop.[16] Despite the impressive results obtained with stressed Ge:Ga photoconductor arrays, it is clear that an extension to longer wavelength that can be achieved without massive stress harnesses would be advantageous. This will be especially relevant for large arrays. The Ge:XX BIB detector shows promise in fulfilling this requirement.

2.3. Bulk photoconductor fabrication

It is worthwhile to give a brief summary of the fabrication steps leading to a state-of-the-art bulk photoconductive detector because it offers a baseline against which BIB detector fabrication can be compared. Essentially all the technology needed to fabricate Ge:XX photoconductors had been developed for completely different applications. The growth of bulk crystals with net-dopant concentrations lower than 10^{10} cm^{-3} was developed for p-i-n diode gamma ray detectors.[17] It was this ultra-pure crystal growth technology which made possible the control of the minority dopant concentration down to the 10^{10} cm^{-3} range. As it turned out, such small minority dopant concentrations lead to impact ionization at very low applied electric fields, in turn leading to small signals. Optimal minority dopant concentrations are close to 10^{12} cm^{-3}.

The majority dopant concentration had to be judiciously chosen to provide significant photon absorption while keeping hopping conduction at an acceptable level. Optimal majority dopant concentrations for shallow acceptors and donors in Germanium lie close to 10^{14} cm^{-3}. Dark currents as low as 100 electrons per second at 2 K have been measured for optimally doped Ge photoconductors.[4] Currents as low as this are required for very low background applications with long current integration times.

Contacts are formed by boron ion implantation for p-type and phosphorus ion implantation for n-type Ge photoconductors. Again, the ion implantation technology has been developed for a wide range of semiconductor applications, especially for silicon related technologies. Thermal annealing restores single crystallinity and activates the implanted atoms. Metallization with a thin 200 Å Pd adhesion layer followed by a few thousand Å of Au completes the contact formation process. Such degenerately doped contacts establish free majority carrier reservoirs at opposite sides of the IR active bulk material. These reservoirs can be cooled to any temperature without freezing out because they are metallic in nature. Furthermore, they make an excellent contact to the metal overlayer because they offer efficient free carrier tunneling between the metal and the implanted semiconductor.

Concluding this section on bulk semiconductor photoconductors, it is important to note that the basic material and fabrication technologies existed before the need for high performance photoconductors arose. This, in no way, should diminish the efforts required to arrive at the results we have today. Rather, it is an observation relevant to the following sections which describe BIB detectors for which new science and technologies had to be and still need to be developed.

3. GERMANIUM BIB DETECTORS

3.1. The BIB detector concept

The Si BIB detector was invented by Petroff and Stapelbroek[18] in 1984. In place of one uniform, moderately doped piece of single crystal semiconductor, we deal with a two layer structure consisting of a pure undoped blocking layer which is a few micrometers thick and a tens of micron thick, heavily doped IR absorbing layer. These two sections are contacted by degenerately doped, ohmic layers. Like bulk photoconductors, BIB devices are unipolar (either all n-type or all p-type). Figure 1 shows the band structure and a sketch of the real structure of an n-type BIB device.

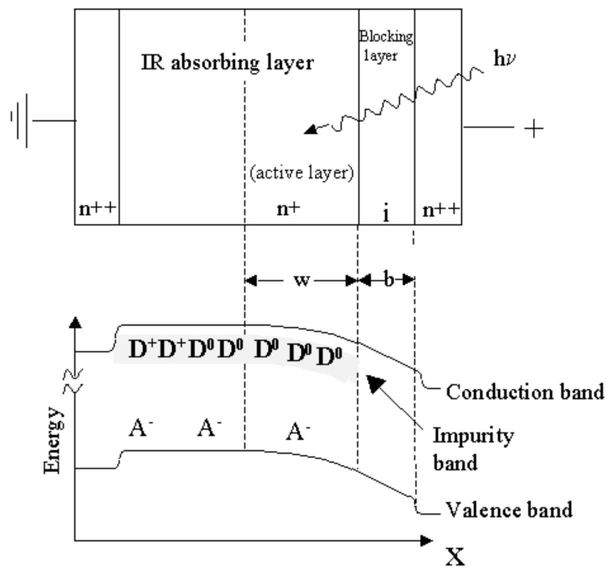


Figure 1: (a) Schematic of an n-type Blocked Impurity Band detector and (b) band diagram shown for a device with an electric field applied. Heavily doped contacts are labeled n^{++}. D^+ = ionized donor, D^0 = neutral donor, A^- = ionized acceptor, w = depletion width.

The asymmetry in structure leads to an asymmetry in the current-voltage characteristics. With positive bias applied to the undoped blocking layer (thickness b), a space charge builds up, beginning at the doped layer-undoped layer interface. Electrons traveling from the left n^+-contact towards this interface will neutralize the small concentration of ionized majority donors which are present because of unavoidable residual acceptors. These compensating negatively charge acceptors, N_A, remain charged, representing the space charge. Increasing the applied bias V_b will widen the space charge region w:

$$w = \sqrt{\frac{2\varepsilon\varepsilon_0(V_b - V_{bi})}{eN_A} + b^2} - b\,, \qquad (6)$$

with ε = relative dielectric constant (16 for Ge), ε_0 = permittivity of vacuum, V_{bi} = built-in voltage (of the order of a few meV), e = charge of the electron.

There are three advantages of a BIB detector compared to a bulk photoconductor. First, the doping concentration in the IR active layer can be increased by ~ 100 (in Ge from 10^{14} cm^{-3} to 10^{16} cm^{-3}) without causing hopping conduction problems because of the blocking layer. This doping increase allows a corresponding decrease in detector volume, effectively reducing interference from energetic particles or photons. Second, the high doping leads to the formation of a donor band which reduces the minimum energy required to transport an electron from the donor band to the conduction band. This in turn leads to longer wavelength response. Third, following a donor ionization event by a far IR photon, the electron travels to the positive contact traversing the blocking layer while the positive donor state (not the donor itself) travels to the undepleted region which is effectively the negative contact. The net result is equivalent to one carrier traveling the full distance between the two contacts, independent of the location of the ionization event. A constant photoconductive gain of unity results, in turn reducing the generation-recombination noise. These advantages have been verified experimentally to a large extent in Si-based BIBs. It is expected that Ge BIB detectors which are emerging will show the same advantages.

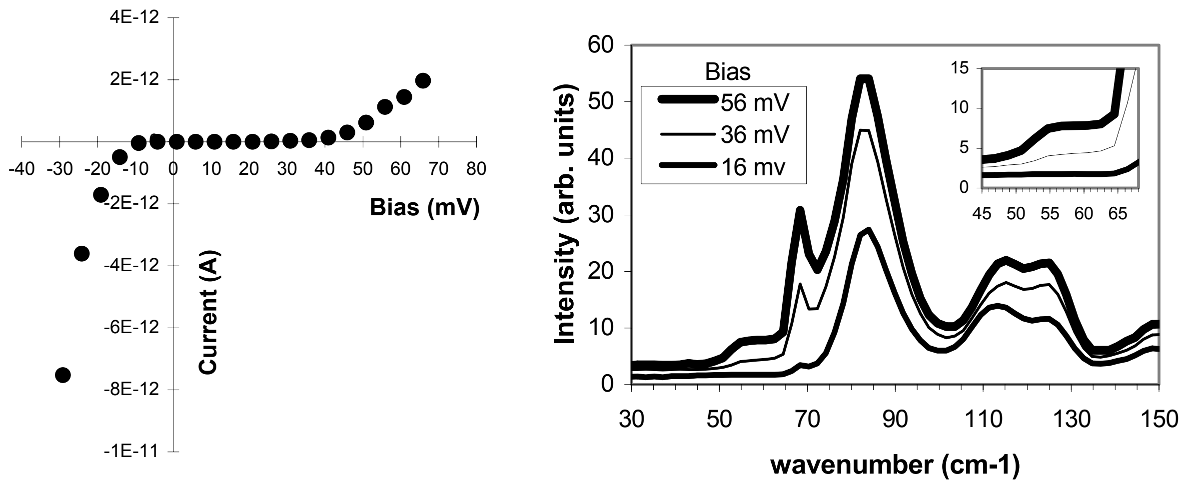
3.2. Ge BIB development

In sharp contrast to bulk Ge photoconductors, a significant materials development for Ge BIBs is required. In the early stages of this development, it was naively assumed (by us and others!) that a BIB technology transfer from Si to Ge would be relatively simple. However, the art and the science of Ge epitaxy was not nearly as far developed as for Si and it was also very different in many respects. The difficulties in achieving blocking layers ten to one hundred times purer than required for Si BIBs and in reducing the minority dopant concentration in the IR active layer again by similar factors were underestimated. Further unknown difficulties arose from the residual impurities in the feed gases needed for CVD growth of the pure and doped Ge layers (GeH_4 or $GeCl_4$). Lastly, Ge epitaxy turned out to be complex and in many ways very different from Si epitaxy. It suffices to observe that all of the early attempts at growing the necessary layers with CVD met with very limited success. The feed gases were too dirty and could not be cleaned up by simple means and the growth temperatures required to obtain good crystallinity were too high which is equivalent to "dirty."

The only way out of this situation is to resort to a simple and not widely practiced epitaxy growth technique called liquid phase epitaxy (LPE). LPE is a solution growth process which makes use of the change in solubility of a semiconductor in an appropriate solvent with temperature. Choosing ultra-pure Pb as a solvent, we began LPE growth research. Pb was chosen because of its low solubility in Ge and because as a group IV element, it does not dope Ge. The first layers turned out to be phosphorus doped around 10^{16} cm^{-3}. Phosphorus was identified with photothermal ionization spectroscopy.[19] Extensive efforts were undertaken to purify the lead (Pb).[20]

Distillation of the solvent (Pb) and high temperature vacuum baking of the graphite crucible resulted in a close to thousand-fold reduction of the P concentration in the Pb solvent. Layers grown from purified lead show that the majority donor concentration was now 5×10^{13} cm^{-3}, and the residual minority acceptor concentration was of the order of 5×10^{12} cm^{-3}. At this stage, we had to abandon our plans to develop p-type Ge BIB devices because the P concentration was too high to obtain sufficient depletion in a p-type IR active layer. N-type Ge BIBs became feasible as long as an IR active layer was grown on an ultra-pure substrate which, after growth, could be thinned down to form the blocking layer. Bandaru recently made excellent progress in this effort.[21] She grew 10^{16} cm^{-3} Sb doped LPE layers on ultra-pure <111> Ge substrates. Using spreading resistance measurements on her layers, she found strong Sb segregation towards the top (last grown) end of the epilayer. Removal of 10 μm resolved this problem. A further imperfection was found at the blocking layer-IR active layer interface. During growth of the doped IR active layer, Sb donors diffused into the blocking layer to a depth of 1.5 μm. This, in turn, leads to an unfavorable electric field distribution as modeled by Haegel et al.[22] This shortcoming will have to be resolved by choosing a more slowly diffusing donor species (perhaps Bi) or by starting the LPE growth run at a lower temperature at the cost of obtaining a thinner layer.

Despite these shortcomings, Bandaru was able to fabricate the first Ge BIBs simultaneously showing several of the characteristic features of such devices, such as an asymmetric I-V characteristic and extended wavelength response (Fig. 2). Assessing the current Ge BIB situation, we can state that the first devices showing the major characteristics have been fabricated. Before fully functional Ge BIBs become available, further purification of the metal solvent used in LPE is needed. We hope that Pb can be purified to a sufficient level, or perhaps other metals will have to be considered (e.g., Sn). In addition, the interdiffusion at the doped-pure interface has to be reduced. All of the common group III acceptors have smaller diffusivities than the group V donors, favoring p-type Ge BIBs. Such Ge BIB detectors will work only if the donor minority concentrations can be lowered in the IR active region to ~ 10^{12} cm^{-3}. Passivation of the free Ge surfaces may become important once large array development becomes feasible. At that point, scaling up of the LPE reactors will also become necessary.



(a) (b)

Figure 2: (a) Dark current – voltage characteristics of a Ge:Sb BIB detector at 2 K. At very low bias the dark current is below the detection limit for the electronics.(b) Spectral response of the BIB detector at 2 K with increasing applied bias. The inset shows an enlargement of the long wavelength onset in photoconductive response and its extension with applied bias.

Many important details, including LPE layer morphology and its dependence on substrate orientation, transparent contact formation, optimal dopant concentration, to name a few, are not discussed here but are treated in detail in the PhD thesis of Jordana Bandaru[21] and in her recent publications.[1,23,24] Further details are given in the paper by S. Goyal et al.[25]

4. GaAs BIB DEVELOPMENT

4.1. The case for n-type GaAs BIB detectors

The major reason to pursue GaAs BIB research and development is the promise of a photoconductive onset at ≥ 300 micrometers. This is based on the fact that the donor binding energy is very close to 6 meV (~ 50 cm^{-1}, 200 μm) and that the 1s groundstate to 2p bound excited state transition energy is ~ 4.3 meV (~ 35 cm^{-1}, 286 μm). Formation of a donor band will easily push out the onset to beyond 300 micrometers. Further factors in support of GaAs BIB development are the use of LPE for GaAs-based light emitting diode manufacturing (though this is done at very high dopant concentrations!) and the availability of 8-nines pure (99.999999%) Ga, the metal solvent of choice for GaAs LPE.

Compared to elemental semiconductors (Ge, Si), one encounters difficulties which are due to the compound nature of GaAs. Any deviation from perfect stoichiometry will lead to large concentrations of native defects (such as vacancies, interstitials and antisites of both host lattice species). These defects are typically charged and form deep level centers. The group IV impurities are amphoteric, i.e., they form shallow donors on Ga sites but shallow acceptors on As sites. This can lead to changes in type within an epilayer depending on the temperature dependence of the site preference. Last but not least, As has a relatively high vapor pressure that may lead to stoichiometry problems if not properly controlled.

4.2. LPE growth of GaAs layers

In the interest of the highest possible purity, we have constructed the most simple tipping boat LPE GaAs reactor based on the design by Bauser et al.[26] The number of parts is small and all can be cleaned thoroughly. The major components are a silica tube enclosure and an ultra-pure graphite crucible which can be rotated by 160 degrees at high temperature. The design and the major results are described in the presentation by Cardozo et al.[10]

We summarize here the major points. Using extensive high temperature (~ 1500 °C) carbon crucible baking cycles, it has become possible to routinely grow epilayers, up to 100 micrometer thick, epilayers with $N_D - N_A \sim 5\times10^{12}$ cm^{-3}. At such purity levels, shallow donors and acceptors are present at similar concentrations and layers with p-type and n-type regions of varying size occurring. These layers have been characterized with capacitance-voltage techniques, while the uniform layers can be analyzed with standard Hall effect measurements.

We feel that these purity levels suffice for both the blocking layer as well as the minority impurity concentration in the IR active layer. The next step will focus on the growth of a set of differently donor doped layers in order to determine the optimal donor doping concentration for the IR active layer. Once this has been achieved, the growth of a doped on a pure layer or vice versa has to be explored. As in the case of Ge, interdiffusion may cause problems.

Assuming that our small scale attempts will be successful, scaling up to LPE growth with the centrifuge installed at the UC Berkeley Physics Department will become feasible.[27,28] The complexity of this tool will require extensive growth studies. The promise of large diameter epi wafers and the possibility to grow sequentially several differently doped layers during the same growth run, makes this approach attractive. The effort and the time required to achieve working GaAs BIB structures should, however, not be underestimated!

5. InAs AND InSb: FUTURE PHOTOCONDUCTOR MATERIALS

The search for longer wavelength response extrinsic semiconductors with electron (hole) binding energies which are lower than in GaAs leads naturally to the compound III-V semiconductors InAs and InSb. Both compounds have exceptionally low electron effective masses which result in very small electron binding energies[29,30] of ~ 1.4 meV for InAs and ~ 0.7 meV for InSb. The photoconductive onset for these two compounds are 886 micrometers and 1772 micrometers, respectively! Low binding energies are synonymous with large Bohr orbits which in turn lead to very low critical concentrations for the metal-insulator transition, $\leq 10^{14}$ cm^{-3} for InSb and slightly higher for InAs. The quality of currently available InSb bulk crystals and of thin films is not sufficient to obtain donor freeze-out at low temperatures, necessary for making a photoconductor. Applications of a small magnetic field sufficiently shrinks the wave function leading to a freeze-out at low temperature. The purest InAs epilayers show signs of freeze-out characteristics without magnetic fields.

It may well be worthwhile to mount a focused effort at exploring the ultimate purity obtainable with InAs and InSb. From simple scaling arguments, we estimate that net-donor concentrations in the range of 10^{12} cm^{-3} to 10^{13} cm^{-3} should lead to samples with significant donor freeze-out, making possible photoconductor detectors. Residual acceptor concentrations 10 to 100 times lower should lead to free carrier lifetimes large enough for photoconductive gains near unity. The very large electron mobilities are advantageous in this respect [see equation (2)]. Based on our experience with LPE GaAs, such donor and acceptor concentrations appear to be attainable.

6. SUMMARY

The major points of this review can be summarized as follows:

– Bulk Ge: XX photoconductors, both unstressed and stressed, with excellent performance have been developed and are widely used in many ground based, airborne and satellite missions. Extensive modeling of the photocurrent signal has led to a quantitative understanding of various time dependent phenomena. The science and technology required for bulk photoconductors was adapted largely from other areas of semiconductor device applications.

– Germanium BIB detector development has reached the point where prototypical devices have been demonstrated. Further efforts in epitaxial growth of the blocking layer and the IR active layer are required. Array development will need scaling up of the currently used equipment. The technology and some crystal growth science could not be borrowed from other applications. This in turn has made BIB development significantly more taxing and time consuming.

– GaAs BIB detectors hold the promise of photoconductive response to wavelengths beyond 300 micrometers. A major achievement is the reproducible growth of LPE layers with $|N_D – N_A| \leq 10^{12}$ cm^{-3}. The optimal donor doping concentrations for the IR active region has to be determined with a series of doping experiments. Interdiffusion between the doped and undoped layers has to be characterized and controlled. Scaling up with a LPE growth centrifuge will require significant time and effort.

– InAs and InSb are semiconductors with extremely small electron effective masses and correspondingly small donor binding energies. At this point in time, both materials are still too impure to observe standard dopant freeze-out. Exploratory LPE studies to determine the feasibility to reach sufficient purification should be undertaken. Renewed interest in semiconductor alloys involving these compound semiconductors may stimulate industrial efforts towards improving the quality (mostly purity) of In and Sb.

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